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Growth, structure, and magnetic properties Mn-Bi based eutectic systems.

Steven Paul Young

GROWTH, STRUCTURE, AND MAGNETIC PROPERTIES OF Mn-Bi BASED EUTECTIC SYSTEMS

by

Steven Paul Young

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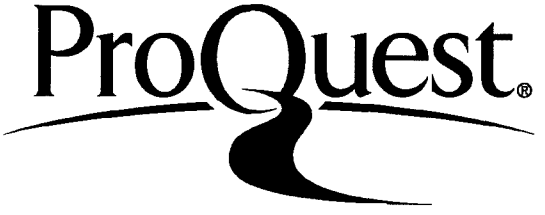

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Professor in Charge

Chairman of Department

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Abstract

The structure and magnetic properties of the directionally solidified MnBi-Bi eutectic are studied for growth rates of 1. and 5. cm/hr. The structure is composed of faceted MnBi rods embedded in a Bi matrix. Improvement in alignment has been achieved over previous work by Boulbes, et al.

Doping effects using ternary Ni additions are investigated for changes in magnetic properties and phase structure. Specimens prepared with up to 20 a/o of the Mn replaced by Ni are ferromagnetic. Higher Mn and Ni levels lead to the appearance of a dendritic phase $Mn_{6.5}Ni_2Bi_4$ with a higher associated volume fraction of ferromagnetic phases.

Magnetic measurements on binary MnBi-Bi eutectics are performed in fields to 12.5 tesla (125,000 Oe) on samples grown during this investigation and on some specimens from Boulbes' previous work. Measurements as a function of temperature, composition, and angle between applied field and growth axis have been made. Angular measurements give a partial test of the Stoner-Wohlfarth (coherent rotation) mode of domain reversal. The constricted nature of the hysteresis loops indicates the presence of multiple magnetic phases. These results are discussed in light of recent studies by Chen and others,

together with current thin foil TEM studies by Shah.

Introduction and Background

Following the report by Heusler[1] on the ferromagnetic nature of manganese bismuth alloys and the determination of the magnetization curve for MnBi by Thielman[2], Guillaud[3] thoroughly investigated the properties of MnBi. The coercive force was found to vary approximately as the inverse of the particle size. A maximum intrinsic coercive force (H_{ci}) of 1.2 tesla (12,000 Oe) was obtained for 3.3 μm mechanically produced powder. Guillaud also measured the anisotropy constant K_1 for MnBi to be 1.16 X 10^6 joules/m^3.

In order to utilize the extremely high anisotropy of MnBi the particles must have parallel easy directions of magnetization.[4] Adams, et al.[5] have calculated the maximum H_{ci} to be 3.5 tesla (35,000 Oe) for aligned particles of 0.8 μm size. The maximum H_{ci} obtained by these investigators due to the clustering and pyrophoric nature of the powder was 0.774 tesla with the 0.8 μm powder. A major drawback to the commercial use of MnBi as a permanent magnet material continues to be the rapid corrosion of the MnBi particles in moist, warm air.

Unidirectionally solidified (UDS) MnBi-Bi eutectic provides an attractive alternative to many of the problems outlined above. The rod type eutectic microstructure allows a fine distribution of MnBi particles

in a non-magnetic Bi matrix. The MnBi particles can be aligned with their easy axis of magnetization parallel to the growth direction without applying external magnetic fields during growth. Particle size is a function of the growth rate and does not depend on mechanical preparation. The MnBi rod phase is protected from atmospheric corrosion by the Bi matrix. The fine particle dispersion of MnBi can be formed, aligned, and protected in what amounts to a one step operation.

Previous investigations with bulk MnBi have identified two ferromagnetic phases with the nominal MnBi composition at room temperature. The first to report the existence of two MnBi phases with different magnetizations and Curie temperatures were Meyer and Taglang.[6] Confirming studies followed by Heikes,[7] Chen and Aagard,[8] Duda and Marchal,[9] Roberts,[10] and Andresen, et al.[11] The low temperature phase (LTP) is stable at room temperature, has a saturation magnetization of about 1.0×10^{-4} Wb-m/kg (80 emu/g), undergoes a first order phase change at 633°K to the paramagnetic state, and has a large positive uniaxial anisotropy. The high temperature phase (HTP) is formed on direct quench to room temperature from above 633°K and is referred to as the quenched high temperature phase (QHTP). This QHTP reverts to LTP on annealing above about 423°K. The HTP is ferromagnetic at room temperature with a Curie

temperature of about 453°K. Although its saturation magnetization is variable, it also possesses a large uniaxial anisotropy. Chen and Stutius[33] have indicated that the difference between LTP and QHTP MnBi may not only be crystallographic but also may be compositional in nature. This will be discussed in a later section.

Studies related to the unidirectional solidification of the MnBi-Bi eutectic and the measuremant of its magnetic properties have now been performed by three separate groups: van Goor and Zijlstra,[12] Yim and Stofko,[13] and Boulbes, et al.[15] ; they agree where the data overlap, but a number of unusual results have been observed. The magnetic studies of van Goor and Zijlstra,[12] carried out below room temperature, led to their proposal of a third MnBi phase with a Curie temperature of about 240°K. More recent magnetic measurements have been made by Boulbes, et al.[15] on samples solidified at different rates between 0.83 and 630 cm/hr. Samples at slower growth rates showed excellent alignment with the alignment degrading somewhat at high growth rates where a planar liquid/solid interface could not be maintained. Specimens of this study showed evidence of what appeared to be at least two magnetic phases. The magnetic properties were quite extraordinary; a specimen grown at 75 cm/hr produced a H_{ci} of 2.4 tesla (24,000 Oe) at 293°K. Clear evidence was observed for a magnetic

component having a H_c^* of 12 tesla (120,000 Oe) and not saturated in an applied field of 14.5 tesla at 77°K. Further studies by Graham, et al.[14] indicated a ferromagnetic-paramagnetic transition at 230°K in good agreement with the observations of van Goor and Zijlstra.[12]

In terms of the application of this eutectic system to commercial magnet use it should be noted that the volume fraction of the ferromagnetic phase MnBi in this eutectic is only ≈5% and some means of increasing the volume fraction is needed, such as through the addition of a ternary element. Also, if there is present more than one magnetic phase, as suggested by the magnetic data, it might be possible to stabilize one phase over the other by the addition of a third element to the Mn-Bi system. The magnetic properties are therefore sensitive to the alignment of the system, the phases present (and their relative amounts), the phase stability, and the volume fraction of the ferromagnetic phase. The purpose of this investigation was to consider each of these factors. The feasability of using the UDS technique to produce a fine dispersion of MnBi rods has been demonstrated by Boulbes;[15] improved alignment was to be sought through a higher thermal gradient and optimum growth rate combination. The effect

†H_c is used to designate the intrinsic coercive force of a component phase.

of ternary additions on phase content, phase stability, and the volume fraction of ferromagnetic material was to be observed. Since previous magnetic measurements were sketchy, this investigation was to make a major effort to measure the magnetic properties of samples grown during this present study at high saturating fields and to remeasure samples grown by Boulbes. This would not only serve to improve the characterization of the system as a whole, but would provide a basis for comparison of new data resulting from varying the growth parameters during directional solidification.

Experimental Procedure

Master Heat Preparation

Specimens of the MnBi-Bi eutectic were prepared from 99.999% bismuth, obtained from the American Smelting and Refining Company or Ventron Materials Corporation, and 99.8% manganese, from the Mining and Metals Division of the Union Carbide Corporation. The doping alloys were 99.% nickel obtained from the International Nickel Company, 99.9% cobalt obtained from Johnson Matthey Chemicals Limited, and 99.8% titanium obtained from Titanium Metals Corporation of America. The phase diagram[33] indicates that the binary eutectic reaction takes place at 535°K (262°C) and at 99.4 w/o bismuth (Figure 1).

Approximately 40 g of the Mn and Bi pellets in the desired proportions of 99.4 w/o Bi and 0.6 w/o Mn were sealed in 6 mm I.D. glass pyrex tubes under vacuum of about 10 μm Hg. Alloy additions were made at the same time in the form of filings produced with a clean steel file. The sealed tubes were placed in an air furnace for one week at 893°K (620°C). This time was needed to insure complete alloying which was slow due to the ever-present thin coating of MnO on the Mn alloying element. Additionally, this time was needed to insure homogenization due to the slow formation of MnBi at the 719°K (446°C) peritectic. The melted specimens were shaken

at least every 24 hours. The 3% expansion of Bi on solidification and cooling caused the tubes to break, so they were placed in an argon atmosphere to prevent oxidation.

Unidirectional Solidification

After all the glass fragments were removed, the master heat ingots were cleaned in methanol and placed in a high purity graphite crucible. This crucible was fabricated in a conical shape to prevent its breakage on solidification, again due to the expansion of Bi. The crucible was purged with argon before insertion of the ingot. The crucible and ingot were placed in the controlled solidification unit shown schematically in Figure 2. This unit is designed so that the furnace and water spray quench are moved while the ingot remains stationary, isolating the sample from any mechanically induced vibration due to the drive mechanism. The initial argon purging and a continuing argon flow during solidification were of the utmost importance. Specimens were remelted for 1.5 hours before beginning solidification. Growth rates of 1. and 5. cm/hr were investigated.

Microstructure Observation

Specimens from each solidification run were cut perpendicular to the growth axis about 5 cm from the end

at which solidification started; other sections were made as needed. After mounting in Buehler Liquid Plastic the specimens were ground on SiC paper to 600 grit followed by polishing on felt laps with 1 μm alumina powder. Scratches were difficult to eliminate due to the soft nature of Bi. Therefore, specimens were electropolished[17] with a mixture of 940 ml of saturated potassium iodide and 60 ml of concentrated hydrochloric acid. A stainless steel cathode was used with contact to the specimen made by a point contact on the polished face; the open circuit voltage was set at 10 volts. After electropolishing for 40 to 60 seconds, the specimens were then lightly polished with 0.3 μm alumina. Contrast between the Bi matrix and the MnBi rods was such that no etchant was required.

Various examination techniques were employed in the course of this investigation. Optical observations were made on a Zeiss Polarizing Microscope with Nomarski interference objectives. Initial higher magnification work was performed on an ETEC scanning electron microscope using only atomic number contrast in place of any etchants; however, this technique is time consuming because it requires critical focusing conditions. Electron microprobe analysis proved to be the simplest and most straightforward examination technique. The ARL microprobe was operated at 20 KV accelerating voltage and 0.05 μA sample current. After polishing and

ultrasonic cleaning, all samples received a thin, vacuum evaporated, carbon coating. Detectors using LiF crystals were employed to produce x-ray scans and x-ray intensity readings for qualitative analysis using MnKα, NiKα, and CoKα radiation. The BiMα radiation was picked up by ADP crystals in the same detectors. Standards for Bi, Mn, Co, and Ni were pure elements: the sample current was set on the Ni standard.

Electron probe analytical data reduction employed the use of the computer program EMPADR VII[18] on a CDC 6400 digital computer. This program is basically an atomic number-absorbtion-fluorescence (ZAF) correction. Although employed primarily for geological analysis, EMPADR VII easily adapts to metallic sample analysis when there are no oxides present. Primary use of the program was in the ternary doped specimens containing Ni. The accuracy of EMPADR VII is maximized by choosing a standard that is close to the unknown in composition. For these ternary analyses, the standard used was composed of a number of point x-ray counts of the MnBi phase of the binary samples. The composition of the data array based on MnBi rods was assumed to be 50 a/o Bi and 50 a/o Mn.

Magnetic Measurements

Magnetic data were obtained at the University of

Pennsylvania using the facilities of the Magnet Laboratory of the Laboratory for the Research on the Structure of Matter. This laboratory is equipped with Bitter type magnets capable of generating steady state fields up to 12.5 tesla (125,000 Oe) in a working space of about 1.6×10^{-5} m^3 (1 in^3). Hysteresis loops were generated in this magnet setup through the use of a vibrating sample magnetometer (VSM) oscillating at 4.2 Hz. A schematic representation of sample and pickup coils is presented in Figure 3.

Calibration of the apparatus with a soft iron sample allowed conversion of the resultant coil voltage to magnetization of the sample. Correlation between kiloamperes magnet current and steady state magnetic field has been made and is a constant for the magnet used. The sensing coils and specimen are entirely encased in a research dewar capable of controlling sample temperature over the range 2°K to 300°K.

Sample size was limited to 3 mm diameter cylinders approximately 8.5 mm in length due to construction of the VSM. Since bismuth is quite brittle, the cylinders were machined on a Materials Research Ltd. S. M. D. Servomet spark machine using brass tubing as the tool. The nature of the cutting technique yielded slightly conical specimens. Samples could be machined such that the cylinder axis could be cut at any predetermined angular

relation to the growth axis.

After weighing, the sample was then cemented to the VSM sample drive rod with Ambroid cement. The VSM sample holder was changed from copper to epoxy when a small pseudo-diamagnetic behavior appeared on the hysteresis loops possibly due to non-uniform eddy current effects with the copper holder. Through the use of a number of different holders, samples cut parallel to the growth direction could be mounted perpendicular or at any other desired angle to the magnetic field. Normally, however, specimens cut parallel to the growth direction were mounted parallel to the magnetic field.

Magnetic data were hand processed using the conversions from graph units to specific quantities based on the previously described calibrations and scale factors. Additionally, graphical separation of magnetic phases was attempted and coercive force and magnetization were plotted against temperature in search of general relationships between the quantities examined.

A summary of the data obtained during this present study is given in the tables of Appendix A. The tables list the sample number, growth rate, intrinsic coercive force, and saturation magnetization for each sample; both room temperature and liquid nitrogen temperature measurements are included. The B-series specimens were grown by Boulbes while the Y-series are the current specimens.

A comment on the factors influencing magnetic measurements made in the course of this investigation is appropriate here. Throughout this study there have been some unexplained changes in coercive force and magnetization in samples grown under seemingly identical conditions. These changes have had the effect of clouding the results of minor changes made during growth to modify the structure and magnetic properties of this system. There are several inherent limitations and other considerations in the system that should be mentioned.

Coercive force is dependent on the size and shape rather than the volume of the particles present. Since it has been observed that the ingots consisted of several grains, the MnBi rods may grow larger in one grain than in the adjoining grain according to the relative ease of nucleation. Smaller rods increase the coercive force approximately hyperbolically[36] so that rod size below a certain level becomes quite critical. Specimens for magnetic measurement are cut from the center of the ingot and, as such, contain a random distribution of grains.

Magnetization is also a function of complex variables. Chief among these variables is the amount of Mn actually dissolved in the specimen. Since it was never possible to remove all of the MnO from the surface of the alloying element, there is some possibility that not all of the Mn added at the outset is completely dissolved.

various instabilities in furnace and quench combine with the above to change the volume of MnBi formed. Total magnetization is volume dependent.

From the magnetics viewpoint, all the samples considered fall under the weakly magnetic classification. This resulted in the need to push the sensitivity of the VSM equipment to the limit. The measurements, nonetheless, remained repeatable.

Result and Discussion

Growth and Structure of MnBi-Bi Binary Eutectics

The binary MnBi-Bi studies were conducted to allow study of growth conditions and to allow optimization of the structure without adding possible compositional conflicts. These studies had the added benefit of proving in new equipment and personnel, and also permitting comparison with previous work.

Growth rates studied were either ca. 1. cm/hr or 4.8 cm/hr. Early growth experiments performed by Boulbes, et al.[15] indicated that oxidation was a problem during the growth operation. Since rod perfection and alignment are of considerable importance to the magnetic measurements, considerable effort was devoted to improve rod alignment and perfection. The early specimens of this study illustrated problems associated with oxidation and alignment. Modifications of furnace design included extension of the hot zone to improve homogenization, redesign of the argon purging system to reduce oxidation, and construction of a heating element allowing direct measurement of the thermal gradient existing at the solid/liquid interface.

The thermal gradient available to Boulbes has been estimated at G~50°K/cm. By contrast, redesign of furnace and quench has allowed a gradient G~200°K/cm in this

study as directly measured with a thermocouple incrementally lowered through the furnace. A sufficiently high thermal gradient is a requisite for coupled growth during directional solidification of a eutectic. Petersen[19] has determined the theoretical line separating coupled growth and dendritic growth for the MnBi-Bi system. The theoretical line follows the stability requirement for coupled growth of eutectic alloys:[20]

$$\frac{G}{R} \geq -m_L \frac{(C_E - C_O)}{D_L} \qquad (1)$$

where G is the thermal gradient at the solid/liquid interface, R is the growth rate, m_L is the slope of the liquidus line, D_L is the diffusion coefficient in the liquid, and C_E and C_O are the eutectic and nominal compositions of the melt. With growth rates between 1. and 5. cm/hr and a thermal gradient of about 200°K/cm, G/R values range from 40 to 200 for the experimental conditions in this investigation; this is well into the coupled growth region determined by Petersen. The main benefit of such a high gradient value is in the flat solid/liquid interface that tends to result. This flat interface results in improved alignment of the MnBi rods in the Bi matrix.

All binary specimens showed structures characterized by MnBi rods embedded in a Bi matrix. The Bi matrix was

not single crystal but typically contained at least two grains in the cross section. The characteristic rodlike structure of this controlled eutectic system has previously been reported by van Goor and Zijlstra[12] and Yim and Stofko.[13] The stability of this morphology has been demonstrated by the lack of structure changes in specimens annealed at $0.9T_m$ for times up to 96 hours: T_m is the absolute melting temperature of the eutectic.

At both growth rates studied, the structure was well aligned and the rods were evenly distributed over the ingot cross section. The alignment of the structure was obtained solely by controlling the rate of heat extraction. This result is in agreement with the findings of Boulbes, et al.[15] but is in contradiction with Yim and Stofko[13] who found it necessary to use an applied magnetic field of 0.05 tesla (500 Oe) during solidification in order to obtain an aligned structure. No measureable magnetic fields were present in the furnace during solidification of ingots in this study. The good alignment achieved can be attributed to the improved growth conditions (improved gradient) and the low solidification rates used throughout. Under these combined conditions, the solid/liquid interface is maintained as flat as possible to minimize divergence of the MnBi rods from the growth axis. It has been shown that the rods tend to grow perpendicular to the interface in rod type eutectics

similar to normal eutectics where lamellae grow normal to the interface.[21]

A representative structure for the specimens grown during the course of this investigation is shown in Figure 4; the growth rate of this specific specimen was 1. cm/hr. Typically, rods were triangular or V-shaped and 1 to 2 μm in cross sectional dimension. Uniform microstructures such as this give an initial indication of the well aligned structure achieved.

Specimens grown at both 1. and 5. cm/hr were used to determine the crystallographic relations between the MnBi rod axes and the growth direction and between the MnBi and Bi phases through the use of thin foil transmission electron microscopy. Shah[22] has determined the orientation of the bismuth phase in these samples to be such that the pseudo 4-fold axis of bismuth (i.e. the <100> type directions for the distorted FCC cell) is in the growth direction ($[\bar{2}\bar{2}01]$ hexagonal notation). The MnBi and Bi phases are related by the planar relation $(\bar{1}\bar{1}20)_{Bi} \parallel (\bar{1}\bar{1}20)_{MnBi}$. The MnBi easy axis of magnetization ([0001]) is parallel to the growth direction.

Since alignment was a critical result of growth parameters, other means were sought to measure the degree of alignment. Magnetic measurements can be used to give an indication of the degree of alignment achieved during unidirectional solidification. Using sample Y-19 grown

at 1. cm/hr, magnetic specimens for this study were machined perpendicular to the growth axis (MnBi rod axis). The sample was then mounted in the VSM sample holder so that it could be rotated with respect to the field, changing the angular relationship between rod axis and magnetic field vector. Figure 5 shows the sample and holder geometry. Figures 6a to 6f† show the family of magnetization versus applied field loops generated as the rod axis was rotated from a 90° angle to the field (rod axis normal to H) to a 0° angle to the field (rod axis parallel to H). At the 0° position 1.5 tesla (15,000 Oe) applied field was necessary to saturate the specimen. This increased to 2.5 tesla (25,000 Oe) at 90° to the field. The minimum at 0° coincides with the easy axis of magnetization of the rods which grow with the C axis parallel to the growth direction. Higher required fields are necessary when this C axis is rotated away from H as expected. This set of curves shows the minimum saturating field at 85° rather than at 90° due to inaccuracy in aligning the specimen in the holder.

Boulbes[15] observed certain abnormalities in the

†To provide maximum clarity with the use of dual units on all graphs, the axes are numerically labelled with the approved SI units only. Additionally, however, the horizontal axis has a dot placed at 100,000 Oe and the vertical axis has a dot placed at 0.5 emu/g to provide an indication of magnitudes for those more familiar with the cgs magnetic units.